FIG. 1

Brinzolamide 4

FIG. 2

$$R_1$$
  $R_2$   $R_2$   $R_3$   $R_4$   $R_4$   $R_5$   $R_5$   $R_6$   $R_6$   $R_7$   $R_8$   $R_8$   $R_9$   $R_9$   $R_9$   $R_9$   $R_9$   $R_9$ 

FIG. 3

## Intramolecular amidation catalyzed by [Ru<sup>II</sup>(TPFPP)(CO)] (1)<sup>a</sup>

Entry	Substrates	Products	Yield (%)
1	OSO <sub>2</sub> NH <sub>2</sub>	HN S O	77
	5	11	
2	OSO <sub>2</sub> NH <sub>2</sub> CO <sub>2</sub> Me	O O O CO <sub>2</sub> Me	76
	6	12 Me	
3	OSO <sub>2</sub> NH <sub>2</sub>	$ \bigcirc $ $ \bigcirc $ $ \bigcirc $ $ N $ $ \stackrel{\circ}{so_2} $	88
	7	(cis)-13	
4	OSO <sub>2</sub> NH <sub>2</sub>	H N-so <sub>2</sub>	61
	8	(cis)-14	
5	OSO <sub>2</sub> NH <sub>2</sub>	HN-SO <sub>2</sub>	56
	9	15	
6	OSO <sub>2</sub> NH <sub>2</sub>	HN.S.O	88
	10	16	

<sup>&</sup>lt;sup>a</sup>Reaction conditions: catalyst: substrate: PhI(OAc)<sub>2</sub> = 0.015: 1: 2; CH<sub>2</sub>Cl<sub>2</sub>, 40°C, 2 h. FIG. 4

High turnover intramolecular amidation catalyzed by  $[Ru^{II}(TPFPP)(CO)]$  (1)

Entry	Substrate	Product	Yield (%)	Turnover
1ª	OSO <sub>2</sub> NH <sub>2</sub>	ON ON O	29	290
2 <sup>b</sup>	OSO <sub>2</sub> NH <sub>2</sub>	$ \begin{array}{c} 11 \\ \stackrel{\text{Me}}{\longrightarrow} 0 \\ \stackrel{\text{N}}{\longrightarrow} 0 \\ \text{(cis)-13} \end{array} $	38	301

<sup>&</sup>lt;sup>a</sup>Reaction conditions: catalyst: substrate: PhI(OAc)<sub>2</sub> = 1: 1000: 2000; CH<sub>2</sub>Cl<sub>2</sub>, 40°C, 20 h. <sup>b</sup>Reaction conditions: catalyst: substrate: PhI(OAc)<sub>2</sub> = 1: 800: 1600; CH<sub>2</sub>Cl<sub>2</sub>, 40°C, 20 h. FIG. 5

## Asymmetric intramolecular amidation catalyzed by $[Ru^{II}(D_4-Por^*)(CO)]^a$

Entry	Substrate	Product	Solvent	Yield (%)	Ee (%) <sup>b</sup>
1	OSO <sub>2</sub> NH <sub>2</sub>	о ни s о	CH <sub>2</sub> Cl <sub>2</sub>	77	46
2		11	$C_6H_6$	63	79
3			$C_6H_6$	48	84°
4	$OSO_2NH_2$		CH <sub>2</sub> Cl <sub>2</sub>	57	71
5		H N-SO <sub>2</sub>	$C_6H_6$	53	81
6			$C_6H_6$	39	82°
7			PhMe	39	77 <sup>d</sup>
8	$OSO_2NH_2$	HN-\$0 <sub>2</sub>	CH <sub>2</sub> Cl <sub>2</sub>	53	69
9			$C_6H_6$	43	82
10			C <sub>6</sub> H <sub>6</sub>	35	87°

<sup>&</sup>lt;sup>a</sup>Reaction conditions: catalyst: substrate: PhI(OAc)<sub>2</sub> = 1: 10: 14; 40°C for 2 h. <sup>b</sup>Ee was determined by HPLC using chiral OD column. <sup>c</sup>Reaction at 4°C and 8 h. <sup>d</sup>Reaction at 0°C and 8 h.

FIG. 6

(1S,2R)-**14** 

17

18

**FIG.** 7